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(54) Title: DETERGENT COMPOSITIONS

(57) Abstract

The present invention relates to a detergent composition comprising a builder system, a nonionic polysaccharide ether and a surfactant system. Said surfactant system comprises an anionic surfactant and a nonionic surfactant at a ratio of from 0.6:1 to 10:1. The compositions of the present invention provide improved soil release performance and clay soil removal performance.

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DETERGENT COMPOSITIONS

Background of the Invention

The present invention relates to detergent compositions comprising a builder system, nonionic polysaccharide ethers and a specific surfactant system for improved greasy soil and clay soil removal.

Field of the Invention

During the fabric laundering operation it is highly desirable to provide the fabrics, particularly man-made fabrics produced from synthetic fibres, with soil release properties and anti-redeposition properties.

A common problem encountered during the laundering process of fabrics is mineral salt deposition. Insoluble salts of calcium may be formed in the wash liquor and be deposited onto the fabric which results in the fabric gaining an undesirable grey and dull appearance. Detergency builders are thus incorporated into detergent compositions in order to reduce this effect by aiding the suspension of such insoluble salts in the wash liquor.

Builders typically employed in detergent compositions include phosphates. However, in some locales a low phosphate formulation is required. In such circumstances the soil suspension of the formulation is reduced and the greying of fabrics is increased.

Another problem commonly encountered during the laundering process is the effective removal of greasy soils. Due to the hydrophobic nature of fabrics composed partially or completely of synthetic fibres, the removal of greasy soils and stains therefrom is particularly difficult. In order to address this problem, soil release polymers may be incorporated into the detergent composition. During

laundering, the soil release agents are adsorbed onto the surface of the fabric, thereby reducing the hydrophobicity of the fabric surface. Once the fabric is treated with a soil release agent, the ease of removal of soils and stains from the surface of the fabric is considerably improved.

The main types of soil release agents incorporated into detergent compositions, which provide benefits to primarily hydrophobic synthetic fabrics include synthetic soil release agents, preferably terephthalate based and polysaccharide ethers.

It has also been observed that the presence of a surfactant system may affect the performance of the polysaccharide ether. Indeed it is known in the art that the performance of the nonionic polysaccharide ethers may be optimised in the presence of nonionic surfactants as the major surfactant species. Indeed, polysaccharide ethers such as cellulose ethers have been described for example in GB 1 534 641, which discloses nonionic surfactant detergent compositions comprising cellulose ether soil release agents such as alkyl and hydroxyalkyl cellulose ethers.

Numerous other examples of such systems have been disclosed in the art. For example, EPO 320296 relates to fabric softening additives for detergent compositions which soften natural fibres without causing redeposition problems on synthetics. An intimate mixture of cellulose ethers and fabric softener at a ratio of 1:1 to 0.06:1 is disclosed. Anionic, nonionic and mixtures of surfactants and phosphate builders are disclosed.

EPO 213730 relates to detergent compositions for treating fabrics which soften natural fibres without causing redeposition problems. The compositions comprise nonionic cellulose ethers, a non-soap anionic detergent (2-50%) and a fabric softening agent. Nonionic surfactants are also disclosed, as are phosphate builders.

EPO 213729 discloses detergent compositions comprising 5-50% soap, 2-25% nonionic surfactants and 0.05-5% cellulose ether which

exhibit improved low temperature solubility and low level soil redeposition. The ratio of soap to nonionic surfactant is 1:1 to 10:1.

EPO 256696 discloses a detergent composition for improved soil suspension comprising anionic surfactants (5-90%), vinyl pyrrolidone polymer and nonionic cellulose ether. Optional ingredients include nonionic surfactants and phosphate builders.

EPO 054 325 discloses detergent compositions with reduced soil redeposition effect comprising a ternary mixture of CMC, carboxylate and cellulose ether with 5-50% detergent active. The actives include anionic and nonionic surfactants and mixtures thereof, but no ratios are specified.

FR 2237960 discloses a detergent composition comprising a cellulose ether and a maleic anhydride copolymer. Detergent actives including anionic and nonionic surfactants, soaps and builders including phosphates are disclosed.

However, the incorporation of nonionic polysaccharide ethers in a detergent formulation, where the surfactant system comprises substantially high levels of nonionic surfactants has been observed to detrimentally affect the soil release performance of the polysaccharides. This problem is further exacerbated in the presence of builder systems comprising reduced phosphate levels. It is believed that the presence of free cations resulting from the use of underbuilt detergent compositions encourage the absorption of the polysaccharide onto soil clay particles present in the aqueous wash liquor. Thus, the amount of polysaccharide available for soil release is reduced. Furthermore, the clay particles containing adsorbed polysaccharide ether readily deposit onto the fabric which results in poorer particulate/clay soil removal performance.

Thus, it is an objective of the present invention to provide a detergent composition comprising a nonionic polysaccharide ether and a surfactant system having improved soil removal performance and reduced clay soil removal negatives.

It has now been found that these objectives may be addressed by the use of a surfactant system comprising a non soap anionic surfactant and a nonionic surfactant at specific ratios. It is believed that the interference of the clay particles with the nonionic polysaccharide ethers may be reduced and the clay soil removal performance of the composition thus improved, by incorporating a specific amount of non soap anionic surfactant with respect to the nonionic surfactant.

Summary of the Invention

The present invention is a detergent composition comprising from 0.01% to 10% of a nonionic polysaccharide ether, a builder system comprising less than 20% of a phosphate builder and at least 1% of a surfactant system, wherein said system comprises a non soap anionic surfactant and a nonionic surfactant at a ratio of from 0.6:1 to 10:1.

All amount, weights, percentages and ratios are given as a % weight of the detergent composition unless otherwise stated.

Detailed Description of the Invention

According to the present invention the detergent composition comprises as essential components a nonionic polysaccharide ether, and a surfactant system comprising non-soap anionic surfactants and nonionic surfactants.

Nonionic Polysaccharide ethers

According to the present invention an essential component of the detergent composition is a nonionic polysaccharide ether. Chemically, the polysaccharides are composed of pentoses or hexoses. Suitable polysaccharide ethers for use herein are selected from cellulose ethers, starch ethers, dextran ethers and mixtures thereof. Preferably said nonionic polysaccharide ether is a cellulose ether. Cellulose ethers are generally obtained from vegetable tissues and fibres, including cotton and wood pulp.

The hydroxy group of the anhydro glucose unit of cellulose can be reacted with various reagents thereby replacing the hydrogen of the hydroxyl group with other chemical groups. Various alkylating and hydroxyalkylating agents can be reacted with cellulose ethers to produce either alkyl-, hydroxyalkyl- or alkylhydroxyalkyl-cellulose ethers or mixtures thereof. The most preferred for use in the present invention are C₁-C₄ alkyl cellulose ether or a C₁-C₄ hydroxyalkyl cellulose ether or a C₁-C₄ alkylhydroxy alkyl cellulose ether or mixtures thereof. Preferably the polysaccharides of the present invention have a degree of substitution of from 0.5 to 2.8, preferably from 1 to 2.5, most preferably from 1.5 to 2 inclusive.

Suitable nonionic cellulose ethers include methyl- and ethyl-cellulose ether, hydroxypropyl-, hydroxybutyl- and hydroxyethyl-methylcellulose ether, hydroxypropyl and hydroxyethyl- cellulose ether, hydroxybutyl methylcellulose ether, ethylhydroxy ethylcellulose ether, hydroxy ethylcellulose ether, methylhydroxy ethyl carboxy methyl cellulose and carboxymethyl hydroxyethyl cellulose.

Most preferably said polysaccharide are methylcellulose ether commercially available such as Metolose (Shin Etsu), ethyl hydroxyethyl cellulose, commercially available as Bermocoll (Akzo/Nobel), methyl hydroxyethyl cellulose ether commercially available as Tylose MH300 (Hoechst) and mixtures thereof.

According to the present invention said polysaccharide ether preferably has a molecular weight from 10000 to 200000, most preferably from 30000 to 150000. The weight average molecular weight is obtained by standard analytical methods as described in Polymer handbooks. A preferred method is light scattering from polymer solutions as originally defined by Debye.

The compositions of the present invention comprise from 0.01% to 10%, preferably from 0.01% to 3%, most preferably from 0.1% to 2% of said nonionic polysaccharide ethers.

Detergent Surfactants

According to the present invention the detergent composition comprises at least 1% of a surfactant system, preferably from 2% to 40% of a surfactant system. According to the present invention the surfactant system comprises as essential ingredients a non soap anionic surfactant and a nonionic surfactant.

Non soap anionic surfactants useful herein include the conventional primary, branched-chain and random C₁₀-C₂₀ alkyl sulphates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulphates of the formula $\text{CH}_3(\text{CH}_2)_x(\text{CHOSO}_3^-\text{M}^+)$ and $\text{CH}_3(\text{CH}_2)_y(\text{CHOSO}_3^-\text{M}^+)$ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulphates such as oleoyl sulphate, the C₁₀-C₁₈ alkyl alkoxy sulphates ("AE_xS"; especially EO 1-7 ethoxy sulphates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), sulphated C₁₀-C₁₈ alkyl polyglycosides, and C₁₂-C₁₈ alpha-sulphonated fatty acid esters.

According to the present invention suitable alkyl or hydroxyalkyl alkoxyated sulphates for use herein are of the formula RO(A)_mSO₃M, wherein R is an unsubstituted C₁₁-C₂₄ alkyl or hydroxyalkyl component, preferably a C₁₂-C₂₀ alkyl or hydroxyalkyl, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl component, A is an

ethoxy or propoxy group, m is from 1 to 15, more preferably from 1 to 10, and M is H or a cation which may be selected from metal cations such as sodium, potassium, lithium, calcium, magnesium, ammonium or substituted ammonium. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations such as tetramethyl-ammonium, dimethyl piperidium and cations derived from alkanolamines, e.g. monoethanolamine, diethanolamine and triethanolamine and mixtures thereof. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulphate, C₁₂-C₁₈ alkyl polyethoxylate (3) sulphate and C₁₂-C₁₈ alkyl polyethoxylate (4) sulphate wherein M is selected from sodium or potassium. C₁₂-C₁₄ alkyl sulphate which has been ethoxylated with an average of from 0.5 to 4 moles of ethylene oxide per molecule is especially preferred.

Other suitable anionic surfactants for use herein include salts (e.g. alkali metal and ammonium salts) of C₁₁-C₂₄, preferably C₁₂-C₂₀ linear alkylaryl sulphonates, particularly linear alkyl benzene sulphonates, primary or secondary alkane sulphonates, alkene sulphonates such as α -olefin sulphonates, ether sulphonates, sulphonated polycarboxylic acids, oxyalkane sulphonates (fatty acid isethionates), acylamino alkane sulphonates (taurides), alkyl and alkenyl sarcosinates, alkyl glycerol sulphonates, fatty acyl glycerol sulphonates, fatty oleyl glycerol sulphonates, and any mixtures thereof.

According to the present invention the compositions comprise from 1% to 80%, preferably from 2% to 50%, most preferably from 3% to 25% of a non soap anionic surfactant.

Nonionic surfactants

According to the present invention another essential component of the surfactant system is a nonionic surfactant.

Nonionic condensates of alkyl phenols

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use herein. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide.

Nonionic ethoxylated alcohol surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. Most preferred are the condensation products of alcohols having an alkyl group containing from 8 to 15 carbon atoms with from about 3 to about 9 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-6.5 (the condensation product of C₁₂-C₁₃ linear alcohol with 6.54 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), NeodolTM 45-4 (the condensation product of C₁₄-C₁₅ linear alcohol with 4 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3 moles of ethylene oxide) marketed by Shell Chemical Company, KyroTM EOBN (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, Dobanol 91 and Dobanol 25 marketed by the Shell Chemical Company and Lial 111 marketed by Enichem.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. Examples of compounds of this type include certain of the commercially-available PluronicTM surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units. The preferred alkylpolyglycosides have the formula



wherein R2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3, x is from 0 to 10 preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 and t is from 0 to 10. The glycosyl is preferably derived from glucose.

Suitable nonionic surfactants for use herein also the C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing.

The compositions of the present invention comprise from 1% to 50%, preferably from 2% to 35%, more preferably from 2% to 30% of said nonionic surfactants.

Preferred surfactants for use herein are linear alkyl benzene sulphonate, alkyl sulphates, alkyl alkoxylated sulphates and alkyl alkoxylated nonionics and polyhydroxyfatty acid amides. According to the present invention the anionic and nonionic surfactant are present in the detergent composition at a ratio of from 0.6:1 to 10:1, preferably from 0.6:1 to 8:1, more preferably from 0.8:1 to 6:1.

The surfactant system of the present invention may optionally comprise zwitterionic, amphoteric surfactants such as C₁₂-C₁₈ betaines, sulphobetaines ("sultaines") and C₁₀-C₁₈ amine oxides and cationic surfactants.

Cationic surfactant

Cationic detergents suitable for use herein are those having one long chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as

alkyldimethylammonium halogenides and surfactants having the formula:



wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of CH_2CH_2 -, $-CH_2CH(CH_3)$ -, $-CH_2CH(CH_2OH)$ -, $-CH_2CH_2CH_2$ -, and mixtures thereof; each R^4 is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH$ - $CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000 and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from about 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Preferred cationic surfactants are the water soluble quaternary ammonium compounds useful in the present composition have the formula:



wherein R_1 is a C₈-C₁₆ alkyl, each of R_2 , R_3 and R_4 is independently C₁-C₄ alkyl, C₁-C₄ hydroxy alkyl, benzyl and $(C_2H_4O)_xH$ where x has a value of from 1 to 5 and X is an anion. Not more than one of the R_2 , R_3 or R_4 should be benzyl.

The preferred alkyl chain length for R_1 is from C₁₂-C₁₅, particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived from synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for the R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds for use herein are:

coconut trimethyl ammonium chloride or bromide; coconut methyl dihydroxyethyl ammonium chloride or bromide; decyl trimethyl ammonium chloride; decyl dimethyl hydroxyethyl ammonium chloride or bromide; C₁₂-C₁₅ dimethyl hydroxyethyl ammonium chloride or bromide; coconut dimethyl hydroxyethyl ammonium chloride or bromide; myristyl trimethyl ammonium methyl sulphate; lauryl dimethyl benzyl ammonium chloride or bromide; lauryl dimethyl (ethoxy)₄ ammonium chloride or bromide and choline esters.

Builder system

According to the present invention the detergent composition comprises as an essential ingredient a builder system. Said builder system comprises less than 20%, preferably less than 10%, more preferably less than 1% phosphate builder. Most preferably the compositions of the present invention are substantially free of phosphate builder. Such phosphate builders include the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, orthophosphates and glassy polymeric meta-phosphates) and phosphonates.

According to the present invention the builder system may comprise non phosphate builders to assist in controlling mineral hardness and the removal of particulate soils. Inorganic as well as organic builders can be used. The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least 1% builder. Liquid formulations typically comprise from 5% to 50%, more typically about 5% to 30%, by weight, of detergent builder. Granular formulations typically comprise from 10% to 80%, more typically from 15% to 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic detergent builders include, but are not limited to, phytic acid, silicates, carbonates (including bicarbonates and

sesquicarbonates), sulphates, and aluminosilicates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) and the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- $\text{Na}_2\text{Si}_2\text{O}_5$ morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- $\text{Na}_2\text{Si}_2\text{O}_5$ (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

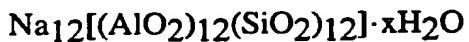
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein w, z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287,

issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylysuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmytysuccinate, 2-dodecenylysuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

Optional ingredients

According to the present invention the detergent compositions may comprise a number of optional conventional detergent adjuncts such as builders, chelants, polymers, antiredeposition agents and the like.

Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionate, triethylenetetra-aminehexacetates, diethylenetriaminepentaacetates, and ethanoldi-

glycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from 0.1% to 10% more preferably, from 0.1% to 3.0% by weight of such compositions.

Polymeric Soil Release Agent

Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C₃ oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C₃ oxyalkylene terephthalate units is about 2:1 or lower, (ii) C₄-C₆ alkylene or oxy C₄-C₆ alkylene segments, or mixtures therein, or (iii) poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2.

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C₄-C₆ alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as MO₃S(CH₂)_nOCH₂CH₂O-, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.

Polymeric soil release agents useful in the present invention also include copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126

(from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group

consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

Bleaching Compounds - Bleaching Agents and Bleach Activators

The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from 1% to 40%, more typically from 5% to 30%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from 0.1% to 60%, more typically from 0.5% to 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Preferred coatings are based on carbonate/sulphate mixtures. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium

monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylarnino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylarnino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Mixtures of bleaching agents can also be used. Peroxygen bleaching agents, the perborates, e.g., sodium perborate (e.g., mono- or tetra-hydrate), the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein. It has also been observed that the incorporation of nonanoyloxybenzene sulphonate in a nonionic polysaccharide ether containing composition (as illustrated in Example 4, II-III) provides an additional colour care performance benefit. It appears that the colour fidelity of certain coloured fabrics when subjected to repetitive washing with a composition comprising NOBS in combination with polysaccharide ethers improves the colour fidelity of the fabrics versus a composition without nonionic polysaccharide ether.

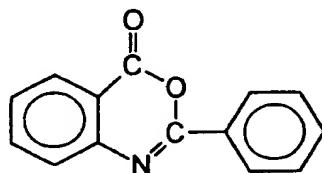
Highly preferred amido-derived bleach activators are those of the formulae:

$R^1N(R^5)C(O)R^2C(O)L$ or $R^1C(O)N(R^5)R^2C(O)L$
wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon

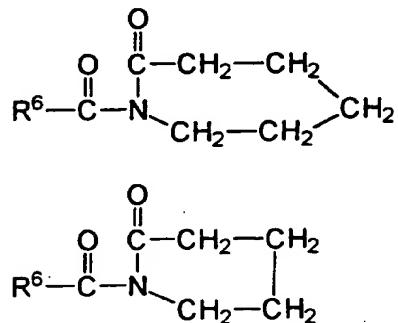
atoms, R⁵ is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydroxyl anion. A preferred leaving group is phenol sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)-oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams, acyl pyrrolidone and acyl valerolactams of the formulae:



wherein R⁶ is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, adsorbed into sodium perborate. Other preferred activators are cationic bleach activators.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from 0.025% to 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $Mn^{IV}2(u-O)3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(PF_6)_2$, $Mn^{III}2(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(\text{ClO}_4)_2$, $Mn^{IV}4(u-O)_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$, $Mn^{III}Mn^{IV}4(u-O)_1(u-OAc)_2\text{-}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_3$, $Mn^{IV}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})\text{-}(\text{OCH}_3)_3(PF_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the

following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; 5,227,084;

Polymeric Dispersing Agents

Polymeric dispersing agents can advantageously be utilized at levels from 0.1% to 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers

of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 90,000, most preferably from about 7,000 to 80,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 70:30 to 30:70. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol or acetate terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyamino acid dispersing agents such as polyaspartate and polyglutamate may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Clay Soil Removal/Anti-redeposition Agents

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain about 0.01% to about 5%.

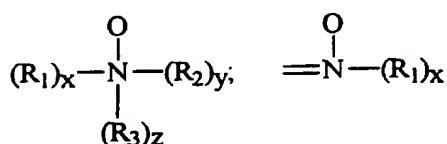
The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Dye Transfer Inhibiting Agents

The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from 0.01% to 10% by weight of the composition, preferably from 0.01% to 5%, and more preferably from 0.05% to 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: $-NC(O)-$, $-C(O)O-$, $-S-$, $-O-$, $-N=$; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $pK_a < 10$, preferably $pK_a < 7$, more preferred $pK_a < 6$.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate

copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

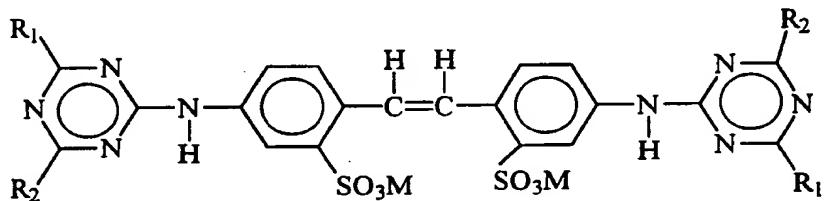
Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched. It has also been observed that additional dye transfer inhibition benefits are provided by compositions comprising nonionic polysaccharide ethers and dye transfer inhibitors such as PVNO and PVPVI such as illustrated in Example 1, reference B and formulation B. It is believed that a synergic effect due to the combination of polysaccharides and dye transfer inhibitors provides the unexpected whiteness maintainance performance benefits to white fabrics which have been subjected to repetitive washing.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000.

PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits,

rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

According to the present invention the detergent composition may comprise any other ingredients commonly employed in conventional detergent compositions such as suds suppressors, softeners, brighteners, additional enzymes and enzyme stabilisers.

The compositions of the present invention may be used in laundry detergent compositions, fabric treatment compositions and fabric softening compositions in addition to hard surface cleaners. The compositions may be formulated as conventional granules, bars, pastes, powders or liquids. The detergent compositions are manufactured in conventional manner, for example in the case of powdered detergent compositions, spray drying, agglomeration or spray mixing processes may be utilised.

Preferably granular detergent compositions according to the present invention have a density of from 400g/l to 1200g/l, more preferably from 500g/l to 1000g/l, most preferably from 600g/l to 1000g/l.

The mean particle size of the components in accordance with the invention should preferably be such that no more than 5% of the particles are greater than 1.7mm in diameter and not more than 5% are less than 0.15mm in diameter.

The combination of the mix of the polysaccharide ether and anionic and nonionic surfactant are present at at least 10ppm in the aqueous wash solution having a pH of from 7 to 11, preferably from 9 to 10.5.

The present invention also relates to a method of laundering fabrics which comprises contacting said fabric with an aqueous laundry liquor containing conventional detergents described herein in addition to the nonionic polysaccharide ether and nonionic and anionic

surfactants of the present invention. In a preferred method polyester and polyester-cotton blends fabrics are used.

Examples

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

XYAS	: Sodium C _{1X} - C _{1Y} alkyl sulphate
25EY	: A C ₁₂₋₁₅ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
XYEZ	: A C _{1X} - C _{1Y} predominantly linear primary alcohol condensed with an average of Z moles of ethylene oxide
XYEzs	: C _{1X} - C _{1Y} sodium alkyl sulphate condensed with an average of Z moles of ethylene oxide per mole
TFAA	: C _{16-C₁₈} alkyl N-methyl glucamide.
Silicate	: Amorphous Sodium Silicate (SiO ₂ :Na ₂ O ratio = 2.0)
NaSKS-6	: Crystalline layered silicate of formula δ-Na ₂ Si ₂ O ₅
Carbonate	: Anhydrous sodium carbonate
MA/AA	: Copolymer of 30:70 maleic/acrylic acid, average molecular weight about 70,000.

Zeolite A	: Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 1 to 10 micrometers
Citrate	: Tri-sodium citrate dihydrate
Percarbonate	: Anhydrous sodium percarbonate bleach coated with a coating of sodium silicate ($\text{Si}_2\text{O}:\text{Na}_2\text{O}$ ratio = 2:1) at a weight ratio of percarbonate to sodium silicate of 39:1
CMC	: Sodium carboxymethyl cellulose
DETPMP	: Diethylene triamine penta (Methylene phosphonic acid), marketed by Monsanto under the Tradename Dequest 2060
PVNO	: Poly (4-vinylpyridine)-N-oxide copolymer of vinylimidazole and vinylpyrrolidone having an average molecular weight of 10,000.
Smectite Clay	: Calcium montmorillonite ex. Colin Stewart Minchem Ltd.
Granular Suds Suppressor	: 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form
LAS	: Sodium linear C_{12} alkyl benzene sulphonate
TAS	: Sodium tallow alkyl sulphate
SAS	: $\text{C}_{12}\text{-C}_{14}$ secondary (2,3) alkyl sulfate in the form of the sodium salt.

SS	: Secondary soap surfactant of formula 2-butyl octanoic acid
Phosphate	: Sodium tripolyphosphate
TAED	: Tetraacetyl ethylene diamine
PVP	: Polyvinyl pyrrolidone polymer
HMWPEO	: High molecular weight polyethylene oxide
MC	: Methyl cellulose ether with molecular weight from 110000 to 130000, available from Shin Etsu Chemicals under the tradename Metolose
HMEC	: Tylose MH300, available from Hoechst
EHEC	: Bermocoll E230, available from Berol/Akzo
EDDS	: [s,s] ethylene diamine disuccinate
HEDP	: 1,1 hydroxyethane diphosphonic acid
Sulphate	: Sodium sulphate
PEO	: Polyethylene oxide ml. wt. 5MM
DHAC	: Dimethyl hydroxyethyl ammonium chloride
TAE 25	: Tallow alcohol ethoxylate (25)

Example 1

The following laundry detergent compositions reference A, formulation A, reference B, formulation B were prepared. Formulation B is according to the present invention.

	Reference A	Formulatio n A	Reference B	Formulatio n B
C45AS/AE3S	6	6	8.6	8.6
C25E3	6	6	-	-
C45E7	6	6	-	-
C24E5	-	-	4.8	4.8
SKS6	-	-	12	12
Zeolite A	38	38	10	10
PVNO	-	-	0.03	0.03
HEDP	-	-	0.8	0.8
Carbonate	7	7	8	8
Percarbonate	14	14	22	22
Savinase TM (4 kNPU)	2	2	2	2
Lipolase TM (100 kLU)	0.2	0.2	0.4	0.4
Suds suppressor	2	2	1.5	1.5
Silicate	3	3	-	-
TAED	6	6	5	5
EHEC	-	0.5	-	0.5
Miscellaneous /Balance	100	100	100	100

Soil removal testing was conducted in a Hotpoint washing machine, short cycle, at 40°C, Newcastle city water with hardness of 12dH, using 75g of the detergent composition. The cotton and polycotton fabrics were first pretreated with each one of the compositions described above and using the condition outlined above. The staining mixtures were evenly spread over the fabric with a brush and left to dry on a bench overnight. The fabrics were then washed using the same formulation.

Differences in greasy soil removal performance are recorded in panel score units (psu), positive having a better performance than the reference product. The following grading scale (psu grading) was used:

- 0 = equal
- 1 = I think this one is better
- 2 = I know this one is a little better
- 3 = This one is a lot better
- 4 = This one is a whole lot better

Grading was done under controlled light conditions by expert graders. The number of replicates used in this test was six. 's' denotes that the observed difference is statistically significant at a 95% confidence level. The significance of the differences between the formulations was obtained using a two way ANOVA calculation. Thus, the differences between the formulations and the differences between replicates were separately calculated using their corresponding variances and the difference was analysed using the F test.

PSU	Reference A	Cotton	substrate	
		Formulatio n A	Reference B	Formulatio n B
Anionic: nonionic ratio	0.5	0.5	1.8	1.8
Average greasy stain	0	0.2	0	+1.1
Ragu*	0	-0.25	0	+0.4s
Pizza**	0	-0.5	0	+0.4
Tuna***	0	-0.1	0	+1.3s
Curry****	0	+1.7	0	+2.2s
Clay soil	0	-3.1s	0	-1.0

		Polycotton	substrate	
PSU	Reference A	Formulation A	Reference B	Formulation B
Anionic: nonionic ratio	0.5	0.5	1.8	1.8
Average greasy food stain	0	-0.6	0	+0.4
Ragu*	0	-0.8	0	+0.6s
Pizza**	0	-1.4	0	-0.1
Tuna***	0	+0.9	0	+0.8
Curry****	0	-1.1	0	+0.4
Clay soil	0	-2.2s	0	-0.2

Ragu* : Pasta Sauce.

Pizza**: Pizza topping sauce

Tuna*** : Tuna mayonnaise.

Curry****: Curry sauce.

Example 2: Granular detergent compositions of the present invention

	I	II	III
Blown Powder			
Phosphate	19	-	19
Zeolite A	-	24	
Sulphate	9	6	13
MA/AA	2	4	2
LAS	6	8	11
TAS	2	-	-
Silicate	7	3	3
CMC	1	1	0.5
Brightener	0.2	0.2	0.2
DETPMP	0.4	0.4	0.2
Spray On			
AE7	2.5	2.5	2.0
AE3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate	6.0	13.0	15.0
PB4	18.0	18.0	10
PB1	4.0	4.0	0
TAED	3.0	3.0	1.0
Zinc Phtalocyanine encapsulate	0.02%	0.02%	0.02%
Savinase protease(TM) (4.0 KNPU / g)	1.0	1.0	1.0
Lipolase lipase (TM) (100.000 LU/l)	0.4	0.4	0.4
Termamyl amylase)TM) 60KNU/g	0.25	0.30	0.15
MC	0.5	-	0.5
HMEC	-	0.5	-
Dry mixed Sulphate	3.0	3.0	5.0

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Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
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Example 3: Granular detergent compositions

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	-
Sulphate	0.0	5.0	-
LAS	3.0	3.0	-
DETPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
45AS			11.0
LAS	6.0	5.0	
TAS	3.0	2.0	
Silicate	4.0	4.0	
Zeolite A	10.0	15.0	13.0
CMC			0.5
MA/AA			2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
AE7	4.0	4.0	4.0
AE3	2.0	2.0	2.0
Dry additives			
MA/AA			3.0
SKS6			12.0
Citrate	10.0	0.0	8.0
Na Bicarbonate	7.0	3.0	5
Na ₂ Carbonate	8.0	5	7
PVP	0.5	0.5	0.5
Alcalase protease TM (3.0 AU / g)	0.5	0.3	0.9
Lipolase lipase TM(100.000 LU/l)	0.4	0.4	0.4
Termamyl amylase TM 60KNU/g	0.6	0.6	0.6
Carezyme cellulase TM (1000CEVU/g)	0.6	0.6	0.6

MC	-	0.6	0.6
HMEC	0.6	-	-
Silicone antifoam granule	5.0	5.0	5.0
Dry mixed Sulphate	0.0	9.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0

Example 4:

Composition	I	II	III
Blown Powder			
Zeolite A	30.0	22.0	6.0
Sulphate	19.0	10.0	7.0
MA/AA	3.0	3.0	6.0
LAS	11.0	10.0	22.0
45AS	5.0	5.0	7.0
Silicate		1.0	5.0
Brightener	0.2	0.2	0.2
Carbonate	8.0	16.0	20.0
DETPMP		0.4	0.4
Spray On			
AE7	3.0	3.0	3.0
AE3			
Dry additives			
PVP	0.5	0.5	0.5
Savinase protease TM (4.0 KNPU / g)	1.0	1.0	1.0
Lipolase lipase TM (100.000 LU/l)	0.4	0.4	0.4
Termamyl amylase TM 60KNU/g	0.1	0.1	0.1
Carezyme cellulase TM(1000CEVU/g)	0.1	0.1	0.1
NOBS		6.1	4.5
PB1	1.0	5.0	6.0
MC	0.4	-	0.4
HMEC	-	0.4	-

Dry mixed Sulphate		6.0	
Balance / Miscellaneous	100	100	100

Example 5:

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sulphate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
DHAC		1.5	1.5
DETPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	2.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
AE7	2.0	2.0	2.0
AE3	2.0		
Dry additives			
Citrate	5.0	0.0	2.0
Na Bicarbonate		3.0	0.0
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PBI	14	7.0	10.0
PEO			0.2
Bentonite			10.0
Savinase proteaseTM (4.0 KNPU / g)	1.0	1.0	1.0
Lipolase lipaseTM (100.000 LU/g)	0.4	0.4	0.4

Termamyl amylaseTM 60KNU/g	0.6	0.6	0.6
Carezyme cellulaseTM (1000CEVU/g)	0.6	0.6	0.6
MC	0.6	-	-
HMEC	-	0.6	0.6
Silicone antifoam granule	5.0	5.0	5.0
Dry mixed Sulphate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0

Example 6:

	I	II
Agglomerate		
45AS	11.0	14.0
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DETPMP	0.4	0.4
Spray On		
AE5	5.0	5.0
Perfume	0.5	0.5
Dry Adds		
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	3.0	1.0
TAED	5.0	7.0
Percarbonate (14.0% AvOx)	20.0	20.0
Terephthalate based soil release polymer	0.3	0.3
Savinase protease TM 4 KNPU/g	1.4	1.4
Lipolase lipaseTM (100,000LU/g)	0.4	0.4

Carezyme cellulase TM (1000CEVU/g)	0.6	0.6
Termamyl amylase TM (60KNU/g)	0.6	0.6
Silicone antifoam particle	5.0	5.0
Brightener	0.4	0.2
MC	0.6	-
HMEC	-	0.6
Balance/ miscellaneous / total	100	100

CLAIMS

1. A detergent composition comprising from 0.01% to 10% of a nonionic polysaccharide ether, a builder system comprising less than 20% of a phosphate builder and at least 1% of a surfactant system, wherein said surfactant system comprises a non soap anionic surfactant and a nonionic surfactant at a ratio of from 0.6:1 to 10:1.
2. A detergent composition according to any one of the preceding claims, wherein said ratio of anionic surfactant to nonionic surfactant is from 0.6:1 to 8:1.
3. A detergent composition according to any one of the preceding claims, wherein said ratio of anionic surfactant to nonionic surfactant is from 0.8:1 to 6:1.
4. A detergent composition according to any one of the preceding claims, wherein said composition is substantially free of said phosphate builder.
5. A detergent composition according to any one of the preceding claims, wherein said builder system further comprises from 10% to 80% of a non phosphate builder selected from silicates, polycarboxylates, carbonates and mixtures thereof by weight of said detergent composition.
6. A detergent composition according to claim 1, wherein said nonionic polysaccharide ether is a cellulose ether, a starch ether, a dextran ether or mixtures thereof.
7. A detergent composition according to claim 6, wherein said polysaccharide is a cellulose ether selected from nonionic C₁-C₄ alkyl-, C₁-C₄ hydroxyalkyl-, C₁-C₄ alkylhydroxyalkyl polysaccharide ethers and mixtures thereof.

8. A detergent composition according to any of the preceding claims, wherein said nonionic polysaccharide ether is a ethyl hydroxyethyl cellulose ether, methyl cellulose ether, methylhydroxyethyl cellulose ether or mixtures thereof.
9. A detergent composition according to any of the preceding claims, wherein said nonionic polysaccharide ether has a molecular weight of from 10000 to 200000.
10. A detergent composition according to any one of the preceding claims, comprising from 0.01% to 3% of said nonionic polysaccharide ether.
11. A detergent composition according to any one of the preceding claims, wherein said anionic surfactant is selected from alkyl sulphonates, alkyl sulphates, alkyl alkoxylated sulphates, alkyl sarcosinates, alkyl alkoxy carboxylates, sulphated alkyl polyglucosides, alkyl alpha sulphonated fatty acid esters and mixture thereof.
12. A detergent composition according to any one of the preceding claims, comprising from 3% to 25% of said anionic surfactant.
13. A detergent composition according to any one of the preceding claims, wherein said nonionic surfactant is selected from polyhydroxy fatty acid amides, ethoxylated alcohols, alkyl polyglucosides and mixtures thereof.
14. A detergent composition according to any one of the preceding claims, comprising from 2% to 20% of said nonionic surfactant.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/07795

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 3/04, 7/00, 11/00, 3/065, 1/12, 1/755; B01J 13/00
 US CL : 252/174.17, 174.14, 550, 553, 135, 534, 315.5, DIG 1, DIG 2,
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/174.17, 174.14, 550, 553, 135, 534, 315.5, DIG 1, DIG 2,

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: detergent, cellulose ether, phosphate, silicate, non-soap(5a)surfactant

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,566,993 (SECEMSKI ET AL) 28 January 1986, col. 1, line 52 to col. 4, line 11.	1-3, 6-7
Y	US, A, 4,174,305 (BURNS ET AL) 13 November 1979, col. 3, line 17 to col. 15, line 12.	1-3, 6-7
Y	US, A, 4,136,038 (PRACHT ET AL) 23 January 1979, col. 2, line 1 to col. 6, line 47.	1-3, 6-7
X	US, A, 4,100,094 (BURNS ET AL) 11 July 1978, col. 2, line 30 to col. 8, line 9.	1-3, 6-7

Further documents are listed in the continuation of Box C.

See patent family annex.

Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"		document defining the general state of the art which is not considered to be of particular relevance
"E"		earlier document published on or after the international filing date
"L"		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)
"O"		document referring to an oral disclosure, use, exhibition or other means
"P"		document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search

20 SEPTEMBER 1995

Date of mailing of the international search report

01 NOV 1995

Name and mailing address of the ISA/US
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/07795

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: 4-5, 8-14 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.